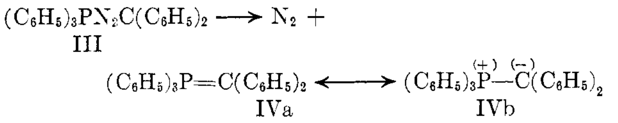
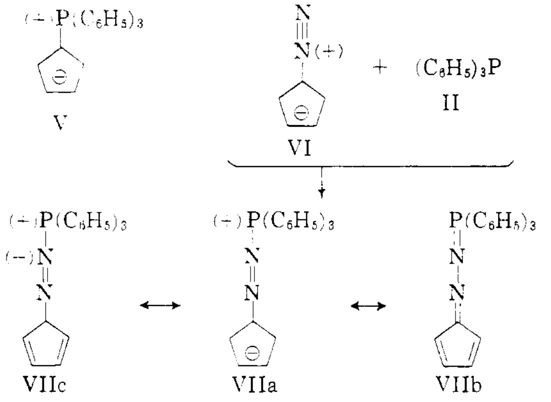


$$\underset{\text{III}}{(C_6H_5)_3PN_2C(C_6H_5)_2} \longrightarrow N_2 + \underset{\text{IVa}}{(C_6H_5)_3P{=}C(C_6H_5)_2} \longleftrightarrow \underset{\text{IVb}}{(C_6H_5)_3\overset{(+)}{P}{-}\overset{(-)}{C}(C_6H_5)_2}$$

We have recently described[4] the preparation of triphenylphosphoniumcyclopentadienylide (V) from triphenylphosphine and the dibromocyclopentenes. It was therefore of interest to investigate the reaction of triphenylphosphine (II) with diazocyclopentadiene[5] (VI) as a new route to the phosphinemethylene V.

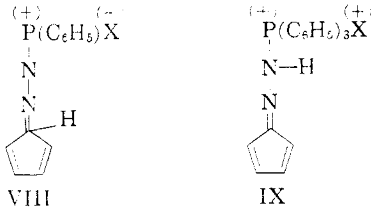
The orange phosphazine VII, m.p. 122–124° was obtained readily and in good yield, but all attempts to effect its thermal decomposition to the phosphinemethylene V have failed.



The ultraviolet spectrum of the phosphazine VII in 95% ethanol exhibits a strong and symmetrical band with maximum at 345 mμ (ε 20,000). This band is absent in the phosphinemethylene V and probably arises from conjugation of the cyclopenta*dienide* and the phosphonium groups through the azo-function —N=N—, by operation of *d*-orbital resonance in phosphorus (VIIa⟷VIIb).

In 95% ethanol solution *containing hydrochloric acid*, the phosphinemethylene[4] V has well defined maxima at 263 mμ (ε10,300), 269 mμ (ε12,100), and 276 mμ (ε11,200). Similar maxima are observed in the spectrum of the phosphazine VII in the same medium. These bands probably correspond to the triphenylphosphonium absorption superimposed on the cyclopentadiene absorption,[4] as in formula VIII for one of the possible tantomeric forms of the protonated phosphazine. The spectrum of the phosphazine VII in acid medium exhibits also a maximum at 295 mμ(ε13,000) not present in the spectrum of the phosphinemethylene V. Interpretation of this spectrum is complicated by the possibility of other tautomeric forms such as the interesting phosphoniumhydrazone IX. It seems clear, however, that no significant hydrolysis of the phosphazine in the acidic aqueous alcoholic medium took place. Staudinger[2] has called attention to the hydrolysis of other phosphazines to the hydrazone and the tertiary phosphine oxide:

$$R_3P{=}N{-}N{=}CXY + H_2O \longrightarrow R_3PO + YXC{=}N{-}NH_2$$



### EXPERIMENTAL[6]

*Diazocyclopentadiene* (VI) was prepared as described by Doering and DePuy[5] and collected at 47–49° (45–48 mm.). *All operations with diazocyclopentadiene should be carried out cautiously. During one preparation, a violent explosion took place after distillation.*

*Reaction of diazocyclopentadiene* (VI) *with triphenylphosphine* (II). A solution of diazocyclopentadiene (VI) (0.90 g.) in petroleum ether (b.p. 30–60°) (3 ml.) was mixed with a solution of triphenylphosphine (II) (2.65 g.) in anhydrous ether (20 ml.). An orange solid separated after a few minutes and was collected after 2 hr., washed with ligroin and dried. Crude weight: 29 g., m.p. *ca.* 117°; the infrared spectrum was identical with that of the analytical sample, m.p. 117–119° (corr.) obtained from methylene chloride–petroleum ether. The phosphazine VII has bands (KBr) at 6.60 (s), 6.75 (m), 6.90 (w), 7.00 (s), 7.45 (m), 9.0 (vs. broad), 10.27 (vs), 10.92 (s), 11.30 (vs), 11.80 (s), and 12.95 (vs) μ. The ultraviolet spectrum in 95% ethanol had $\lambda_{max}$ 345 mμ (ε 20,000), a broad band centered at *ca.* 300 mμ (ε 8,000), three slight maxima at 262, 268, and 275 mμ (ε 6,000) and a shoulder at 220 mμ (ε 36,600). The spectrum in 95% ethanol containing hydrochloric acid had $\lambda_{max}$ 295 mμ (ε 13,600). 278 mμ (ε 15,200), 270 mμ (ε 15,200), 268 mμ (ε 13,000; inflexion), and 225 mμ (ε 30,000).

*Anal.* Calcd. for $C_{23}H_{19}N_2P$: C, 78.0; H, 5.4; Found: C, 78.3; H, 5.7.

The phosphazine VII was heated to 165–175° alone and in the presence of copper powder. The thermal decomposition was also attempted in boiling xylene. No triphenylphosphoniumcyclopentadienylide V could be detected among the tarry decomposition products.

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[4] (a) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957); (b) *J. Am. Chem. Soc.*, **79**, 6167 (1957).

[5] W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

[6] Analysis by Microtech Laboratory, Skokie, Ill.

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## Detection of Thiocarbonyl Groups by Infrared Spectroscopy

E. SPINNER

*Received July 18, 1958*

Until recently only meagre and contradictory information was available concerning the position of thiocarbonyl bands in the infrared,[1] but it has now

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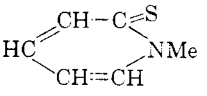
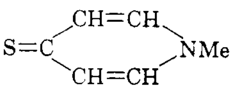
[1] J. I. Jones, W. Kynaston, and J. L. Hales, *J. Chem. Soc.*, 614 (1957).

been established[1,2] that the frequency of the unperturbed thiocarbonyl stretching vibration is 1140 ± 80 cm.$^{-1}$ (in agreement with semiempirical calculation[3]). This frequency is rather insensitive to polar effects, but accidental resonance,[4,5] *e.g.* with the $NH_2$ wagging vibration (~1130 cm.$^{-1}$) in $—CS·NH_2$ derivatives, or with asymmetric N-C-N stretching (1100–1200 cm.$^{-1}$) in $-\overset{|}{N}·CS·\overset{|}{N}-$ derivatives, may give rise to absorption bands in different positions due to "mixed" vibrations.

The applicability of infrared spectroscopy to studies of thiol-thione equilibria such as are at present being pursued in this Department[6] was examined, and conjugated C=S groups have been found to give rise to absorption bands as intense as carbonyl stretching bands. The infrared spectra of I and II have been compared with those of the corresponding carbonyl compounds (O in place of S). Strong absorption in the range 1110–1145 cm.$^{-1}$ is observed in the spectra of the thio-compounds, while the oxo-compounds display only comparatively weak absorption in this region ($\epsilon \leqslant 60$). No other band characteristic of the C=S group, and absent from the spectra of the C=O derivatives, has been found. The maximal intensity observed for II is among the highest recorded for infrared absorption bands.

TABLE I


I


II

FREQUENCIES ($\nu$ in cm.$^{-1}$) AND APPARENT[a] INTENSITIES ($\epsilon_{max}$ IN l. cm. mole$^{-1}$) OF THIOCARBONYL STRETCHING BANDS IN THE INFRARED[b]

| Compound | State | $\nu$ | $\epsilon_{max}$ |
|---|---|---|---|
| I | Soln. in $CS_2$ | 1114, 1142 | 475, 250 |
| I | Soln. in $CCl_4$ | 1117, 1143 | 470, 280 |
| II | Soln. in $CS_2$ | 1127 | 1450 |
| II | Solid in KBr | 1111 | |
| I, H in place of Me | Soln. in $CS_2$ | 1144 | 525 |
| I, H in place of Me | Soln. in $CHCl_3$ | 1143 | (strong) |
| II, H in place of Me | Soln. in $CHCl_3$ | 1126 | (strong) |
| II, H in place of Me | Solid in KBr | 1111, 1122 | |

[a] Not corrected for finite slit widths. [b] Measured on a single-beam single-pass spectrometer.

2- and 4-Mercaptopyridine in aqueous solution have been shown to be principally thiones,[6] *i.e.* I and II with H in place of Me, in analogy with 2- and 4-hydroxypyridine which actually are predominantly carbonyl compounds.[7,8] The data in the table show that these mercaptopyridines are essentially thiocarbonyl compounds also in less polar media. This study is being extended.[3]

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(2) R. Mecke, R. Mecke, and A. Lüttringhaus, *Chem. Ber.*, **90**, 975 (1957), and previous papers cited there.

(3) Details will be reported later.

(4) A. Yagamuchi, *et al.*, *J. Am. Chem. Soc.*, **80**, 527 (1958).

(5) M. Davies and W. J. Jones, *J. Chem. Soc.*, 955 (1958).

(6) A. Albert and G. B. Barlin, *Current Trends in Heterocyclic Chemistry*, Butterworths, London, 1958, p. 51.

(7) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956).

(8) S. F. Mason, *J. Chem. Soc.*, 4874, 5010 (1957).

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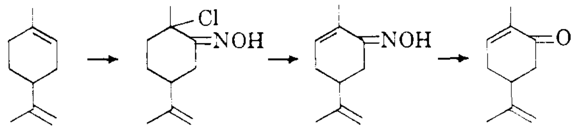
## Nitrosochloride Syntheses and Preparation of Carvone

ROBERT H. REITSEMA[1]

*Received July 21, 1958*

A convenient preparation of limonene nitrosochloride has been developed. In place of the usual generation of nitrosyl chloride in a separate generator or the use of amyl nitrate it has been found that nitrosochlorides can be formed *in situ* by simultaneous addition of sodium nitrite and acid to the olefin. Yields by the procedure are high, and the quality of the product is satisfactory. Limonene nitrosochloride can be produced in yields of 80% with rotations of 226°.



The amount of acid used in the reaction is critical. The usual amount of concentrated aqueous hydrochloric acid used was 40–50 ml. per tenth mole of olefin. As low as 33.3 ml. per tenth mole of olefin gave nearly the same results. Use of 75 ml. of concentrated acid per tenth mole of olefin reduced the yield from the usual 75–80% range to less than 10%. In general, equimolar proportions of sodium nitrite were used although a 50% excess had no adverse effects. The temperature of the reaction had to be maintained below 10°. Operation at 20° resulted in a 26% yield of nitrosochloride. The rate of addition and the efficiency of stirring had to be adjusted to avoid localized heating and high acid concentrations even with optimum amounts of reagents.

Other cyclohexene derivatives can be converted to the nitrosochlorides by the same process. Using the conditions found optimum for limonene, yields

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[1] Present address: The Ohio Oil Co., Littleton, Colo.